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COMPLETE SPECIFICATION

Process for the Removal of Carbon Dioxide from Gases

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a Company organised under the Laws of the Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

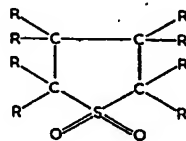
This invention relates to a process for the removal of carbon dioxide from gases which are free or substantially free from hydrogen sulphide.

In the present specification and claims the expression "gas" is used to denote a gaseous or vaporous mixture that contains carbon dioxide and at least one other gas or vapour. As stated, the gases to be treated in accordance with the present invention are free or substantially free from hydrogen sulphide, i.e. their hydrogen sulphide content should be so low as to make a further lowering unnecessary (although such a lowering may be incidentally effected in the course of the present process). The hydrogen sulphide content of the gases to be treated will usually be below 0.5% by volume.

Many processes have already been proposed for the removal of carbon dioxide from such gases. Some of these are based on the use of dilute aqueous solutions of alkanol amines, but in commercial operations these particular solvents have the disadvantage of having a pronounced tendency to corrode processing equipment. Furthermore unduly large proportions of these aqueous solutions are often required in order to obtain a substantial degree of carbon dioxide removal. This implies that the capital and operating expenditures for treating a given quantity of gas are very high. Another disadvantage of many of these known processes is that the solvents used do not selectively remove water at the same time that they absorb the carbon dioxide. Since water cannot be tolerated in many instances in the treated gases it is then necessary to instal separate dehydration equipment. This of course constitutes an additional cost factor in the processing of gases containing appreciable amounts of water.

The process of the present invention overcomes these disadvantages.

According to the invention a process for the removal of carbon dioxide from a gas which is free or substantially free from hydrogen sulphide comprises intimately contacting the gas with a selective solvent comprising a sulphone of the general structure



wherein at least four of the R's are hydrogen and any remaining R's are alkyl groups having from 1 to 4 carbon atoms each.

The said sulphones are based upon cyclo-tetramethylene sulphone, the basic and preferred species being sulpholane (otherwise referred to as thiophene tetrahydro-1,1-dioxide). Suitable derivatives of the basic compound include 2,3-dimethyl cyclo-tetramethylene sulphone; 2,4-dimethyl cyclo-tetramethylene sulphone; 2,5-dimethyl cyclo-

tetramethylene sulphone; 3-ethyl cyclooctamethylene sulphone; 2-methyl 5-propyl cyclooctamethylene sulphone as well as their analogues and homologues. It is preferred that the number of alkyl radicals does not exceed 4 and it is still more preferable that no more than 2 alkyl substituents are appended to the tetramethylene sulphone ring.

The present process has the important advantage that use can be made of a undiluted or substantially undiluted sulphone. The disadvantages associated with the known processes using dilute aqueous solutions of other solvents are not met in the present process. Thus it is possible to obtain a desired degree of carbon dioxide removal with a substantially reduced solvent flow, with concomitant saving in capital and operating expenditures. Furthermore, the essentially dry solvent will, besides selectively absorbing carbon dioxide from the gaseous feed, also absorb water vapour present in the feed and, if a dry feed is charged to the plant, no water will be picked up by the gas from the solvent during the processing, so that the treated gas will also be substantially water-free. A separate dehydration step for the treated gas will generally not be required.

The gases which may be treated in accordance with this invention include refinery and natural gases and also hydrogen-containing gases, such as are obtained in catalytic reforming processes, and gases obtained by partial combustion of hydrocarbons with oxygen-containing gases. The process is particularly suitable for the purification of natural gases having high carbon dioxide contents. These gases, and particularly natural gas, may contain not only substantial amounts of carbon dioxide together with normally gaseous hydrocarbons such as methane and ethane, but may also contain minor proportions of gasoline-range hydrocarbons such as C_4 - C_7 hydrocarbons, while water vapour will practically always be present. However, the gases to be treated in accordance with the present invention must anyhow be free or substantially free from hydrogen sulphide.

The basic step in the process of this invention comprises intimate contacting, preferably countercurrently, between the gas and the sulphone solvent, under a pressure preferably in excess of 7 kg/cm² absolute, e.g. up to 150 kg/cm² absolute or even higher pressures. The temperature at which intimate contacting is effected is not particularly critical; it is preferred to operate between 10°C. and 65°C., more preferably between 25°C. and 50°C. Normally, intimate contacting would take place in a vertically-positioned tower equipped with baffles, trays or similar devices to improve the contact between the gas to be treated and the solvent so that the carbon dioxide is removed progressively from the gas. If desired, heat may be supplied (e.g. by means of a steam coil) near the bottom of the tower, this section being heated to a temperature of e.g. 38°C. to 177°C. Optionally, the tower may be constructed as a rectified contacting zone to maintain a differential in temperature between the top and bottom sections of the tower. The treated gas leaves the tower near or at the top while the fat solvent leaves the tower at or near the bottom.

The resulting fat solution of carbon dioxide and possibly other impurities may be cooled (e.g. through a heat exchanger) and passed to a stripper at substantially reduced pressure of, for instance, 0.15 to 1.75 kg/cm² abs. In the stripper the fat is heated to an elevated temperature to volatilize the absorbed components which will leave the stripper at the top. The bottom of the stripper may be heated, e.g. to a temperature in the range of 150°C. to 205°C., and this may be done by means of a reboiler.

A preferred form of the process according to the present invention comprises the modification of the sulphone with 1 to 10% of a liquid with a relatively low boiling point. Hydrocarbons having from 8 to 12 carbon atoms per molecule are very suitable. The principal purpose of this modification is to facilitate the stripping step to which the fat sulphone is subjected. Since the latter has a relatively high boiling point, it must be heated to a rather high temperature to attain substantially complete removal of absorbed components. A modifying component of the sulphone, such as hydrocarbons having from 8 to 12 carbon atoms, boils at a substantially lower temperature than the sulphone and thus acts as a stripping agent, carrying with it any absorbed components present in the solvent phase.

If hydrocarbons having from 8 to 12 carbon atoms per molecule are used as a stripping aid it is recommended to pass the gases so evaporated through a cool section near the top of the gas stripper. If cooled to approximately 10°C. to 65°C., the vapours of the stripping fluid are condensed and may be returned to the stripped solvent for recycle to the high pressure absorber. The reconstituted lean solvent is then re-pressured on its recycle route to the absorber.

If the gas to be purified contains higher molecular weight hydrocarbons, which will generally be components boiling in the gasoline range, these will usually have been

extracted from the feed in the absorber and will usually be driven off in the stripper. These hydrocarbons may, if desired, be removed from the stripper top gas by scrubbing with a hydrocarbon oil having a somewhat higher boiling range, e.g. a gas oil or lubricating oil.

In the modified sulphone solvent the C_6 — C_{12} hydrocarbons as stripping aid may suitably be replaced by other low boiling liquids such as water. Occasionally the selective action of the physical sulphone solvent may be improved by addition of known chemical solvents, e.g. of the alkanol amine type.

The present process may be carried out in conventional absorber stripper units; a particular embodiment will now be described by way of example with reference to the accompanying drawing. This is a diagram of a plant in which this embodiment, which is very suitable for treating a gaseous mixture containing a large proportion of carbon dioxide, is carried out.

EXAMPLE

A Hydrocarbon feed gas, having a composition as indicated in the table below, is treated with sulfolane, the molar ratio of solvent to feed gas being about 1.6:1. The feed gas enters a high pressure absorber 1 by means of a feed gas line 2 at a temperature between 21 and 32°C. and at a pressure of about 77 kg/cm²abs. The lean solvent (Sulfolane) is injected into the absorber 1 by means of a line 3, treated gas leaves the top of the absorber through a line 4 and the fat solvent leaves the bottom of the absorber by means of a line 5 to enter a flasher 6 wherein the pressure is reduced to 35 to 50 kg/cm²abs., the temperature remaining about the same. In the flasher 6 a small amount (5 to 20%) of the carbon dioxide is flashed off together with any light hydrocarbons absorbed in the solvent. This flashed portion of the absorbed gases is returned through a compressor 7 to the absorber 1 by means of a line 8. The partially flashed sulfolane leaves the flasher 6 by means of a line 9 and passes to a secondary flasher 10 wherein the pressure is reduced to about 8.5 kg/cm²abs. In this flasher the bulk of the carbon dioxide is removed by means of a line 11 and is passed to an expander turbine 12 wherein the gases are expanded to a pressure of about 1.4 kg/cm²abs., thereby driving the turbine which in turn drives a lean solvent pump 13. The expanded gases leave the turbine by means of a line 14 and enter a flashed acid gas outlet 15. The sulfolane, which now contains only a minor proportion of the carbon dioxide, leaves the bottom of the flasher 10 by means of a line 16, and is heated with hot lean sulfolane in a heat exchanger 17 and with steam in a heater 18. It then enters a final flasher 19 at a temperature between 121 and 149°C. Under these conditions any remaining carbon dioxide is flashed off and passes by means of the line 15 via a cooler 20 to the acid gas outlet. In the cooler 20 condensate is collected and recycled to the partially cooled lean solvent through a line 21. The lean solvent leaves the bottom of the final flasher 19 by means of a line 22, via the heat exchanger 17 where it is cooled by the stream leaving the secondary flasher 10, and is then further cooled by the injection of condensate sent by means of the line 21 from the cooler 20. Additional cooling may be applied in an auxiliary heat exchanger 28 before the lean solvent enters the lean solvent pump 13 and is returned through a line 23 to the absorber 1. A bleed stream from the final flasher 19 may optionally be sent by means of a line 24 to a dehydration and clean up column 25 wherein the pressure is still further reduced to 0.07 to 0.14 kg/cm²abs., the lean solvent then being returned by means of the line 3 and a dry solvent pump 26 to the absorber 1 after being at least partially cooled in a cooler 27.

The Table illustrates the results when operating the process as described in the example at a flow ratio (mols) of about 1.6:1.

TABLE

Analyses of feed and products: % by vol.

	Feed*	Treated Gas	Flashed Acid Gas
CO ₂	48.5	1.5	94.3
C ₁	44.2	85.0	2.0
C ₂	3.0	5.5	0.3
C ₃	0.7	1.2	0.2
C ₄ +	0.3	0.4	0.2
N ₂	3.2	6.3	0
N ₂ O	0.07	0.005	3.0

*The feed gas was free from hydrogen sulphide

When treating gases such as hydrogen or nitrogen which are contaminated with acid gases, particularly carbon dioxide, but which do not contain hydrocarbons, the first flashing step and the recycle of the flashed gases to the absorber can be omitted. Furthermore, when treating such gases which are essentially anhydrous when obtained from the usual sources, dehydration or clean up steps are not necessary.

WHAT WE CLAIM IS:—

1. A process for the removal of carbon dioxide from a gas which is free or substantially free from hydrogen sulphide, which comprises intimately contacting the gas with a selective solvent comprising a sulphone of the general formula



wherein at least four of the R's are hydrogen and any remaining R's are alkyl groups having from one to four carbon atoms each.

2. A process as claimed in claim 1 in which the sulphone is a derivative of cyclotetramethylene sulphone with not more than two alkyl substituents having one to four carbon atoms each.

3. A process as claimed in claim 1 in which the sulphone is cyclotetramethylene sulphone.

4. A process as claimed in any of the preceding claims in which the gas to be treated comprises a mixture of normally gaseous hydrocarbons.

5. A process as claimed in any of the preceding claims in which the gas to be treated contains hydrogen.

6. A process as claimed in any of the preceding claims in which the gas to be treated contains components that boil within the gasoline range.

7. A process as claimed in any of the preceding claims in which the intimate contacting is effected at a pressure above 7 kg/cm² absolute.

8. A process as claimed in any of the preceding claims in which the intimate contacting is effected at a temperature in the range 10°C. to 65°C.

9. A process as claimed in any of the preceding claims in which the solvent comprises a sulphone and 1 to 10% by weight of hydrocarbons having from 8 to 12 carbon atoms per molecule.

10. A process as claimed in any of the preceding claims in which the treated gas is separated from the fat solvent.

11. A process as claimed in any of the preceding claims in which the absorbed gases are stripped from the fat solvent under substantially reduced pressure.
12. A process as claimed in claims 9 and 11 in which the stripped gases are cooled to condense C_8 — C_{12} hydrocarbons originating from the solvent and the condensed hydrocarbons are subsequently recombined with the stripped solvent mixture. 5
13. A process for the removal of carbon dioxide from a gas which is free or substantially free from hydrogen sulphide substantially as described with particular reference to the Example and the accompanying drawing.
14. A process for the production of a gas with reduced carbon dioxide content substantially as described with particular reference to the Example and the accompanying drawing. 10
15. A gas purified by a process as claimed in any of the preceding claims.
16. Carbon dioxide obtained by a process as claimed in any of claims 1 to 14.
- KILBURN & STRODE,
Chartered Patent Agents,
Agents for the Applicants.

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COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of
the Original on a reduced scale*

